Optical spin orientation of a single manganese atom in a quantum dot

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A hight degree of spin polarization is achieved for a Mn atom localized in a semiconductor quantum dot using quasi-resonant optical excitation at zero magnetic field. Optically created spin polarized carriers generate an energy splitting of the Mn spin and enable magnetic moment orientation controlled by the photon helicity and energy. The dynamics and the magnetic field dependence of the optical pumping mechanism shows that the spin lifetime of an isolated Mn atom at zero magnetic field is controlled by a magnetic anisotropy induced by the built-in strain in the quantum dots.

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Controlling the interaction between spin polarized carriers and magnetic atoms is of fundamental interest to understand the mechanism of spin transfer. Spin transfer could lead to the development of devices in which the spin state of magnetic atoms is controlled by the injection of a spin polarized current and not by an external magnetic field, as in conventional magnetic memories. Information storage on a single magnetic atom would be the ultimate limit in the miniaturisation of these magnetic memories. The performance of such a device will rely on the lifetime of the isolated spin. Dilute magnetic semiconductors (DMS) systems combining high quality semiconductor heterostructures and the magnetic properties of Mn dopant are good candidates for these ultimate devices [1]. In a DMS, spin polarized carriers introduced by optical excitation couple strongly with localized Mn spins allowing, *e.g.*, photo-induced magnetization to be achieved [2, 3]. It has been known for years that, in the absence of carriers and under magnetic field, highly dilute ensembles of Mn present a spin relaxation time in the millisecond range [4]. However, the dynamics of such ensembles can be much faster at zero field [5]. In addition, very few is known about the zero field dynamics of a single Mn spin, and the optical spin orientation of a single magnetic atom in a solid state environment is still a challenge [6].

We demonstrate a new way to optically address the spin of a single Mn atom localized in an individual quantum dot (QD): the injection of spin polarized carriers under selective optical excitation is used to prepare a non-equilibrium Mn spin distribution without any applied magnetic field. Photoluminescence (PL) transients recorded when switching the circular polarization of the excitation reflect the dynamics of this optical orientation mechanism. The magnetic field dependence of the optical pumping efficiency reveals the influence of the Mn fine structure on the spin dynamics: the strain induced magnetic anisotropy of the Mn spin slows down the relaxation at zero magnetic field. We show that the Mn spin distribution prepared by optical pumping is fully conserved for a few microseconds.

Growth and optical addressing of QDs containing a single magnetic atom were achieved recently [7, 8, 9]. The static properties of these systems are now well understood: when a Mn dopant atom is included in a II-VI QD, the spin of the optically created electron-hole pair interacts with the five d electrons of Mn (total spin S=5/2). This leads to a splitting of the once simple PL spectrum of an individual QD into six $(2S+1)$ components, as shown in the bottom of Fig. 1(a). This splitting results from the spin structure of the confined holes which are quantized along the QDs' growth axis with their spin component taking only the values $J_z = \pm 3/2$ [10]. The hole-Mn exchange interaction reduces to an Ising term $J_z S_z$ and shifts the PL energy of the QD according to the relative projection of the Mn and hole spins [11]. The intensity of each line reflects the probability for the Mn to be in one of its six spin components and it is a probe of the Mn spin state at the moment the exciton recombines [12]. As the spin state of the Mn fluctuates during the optical measurements, the six lines are observed in the time averaged PL spectrum.

To optically pump the Mn spin, the PL of a single QD was quasi-resonantly excited with a tunable continuous wave (CW) dye laser. In order to record the spin transients, the linear polarization of the excitation laser was modulated between two orthogonal states by switching an electro-optic modulator with a rise time of 5 ns, and converted to circular polarization with a quarter-wave plate. Trains of resonant light with variable duration were generated from the CW laser using acousto-optical modulators with a switching time of 10 ns. The circularly polarized collected light was dispersed by a 1 m double monochromator before being detected by a fast avalanche photodiode in conjunction with a time correlated photon counting unit with an overall time resolution $\sim$ 40 ps.

Fig. 1 and 2 summarize the main features of the time-resolved optical orientation experiment. The PL of the exciton-Mn (X-Mn) system was excited in one of the sharp lines observed at slightly higher energy (top of Fig. 1(a)), *i.e.*, in an excited states of the X-Mn complex [13]; the PL intensity was measured in circular polarization (*e.g.*, σ^-, corresponding to the recombination of the -1 exciton). Then, the relative intensity of the six lines

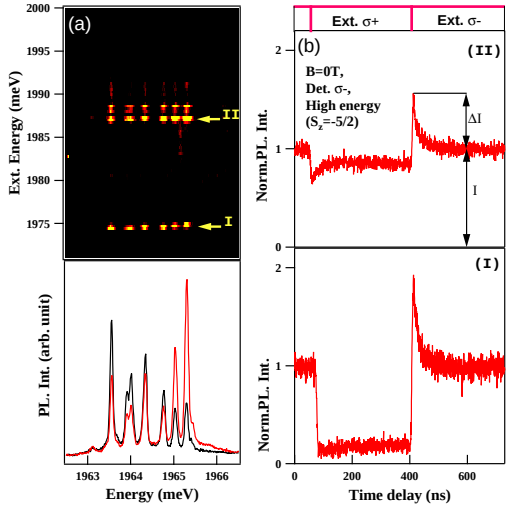

FIG. 1: (Color online) (a) PL and PL excitation spectra of a single Mn-doped QD at $B = 0$ T and $T = 5$ K. The PL is detected in circular polarization under an alternate σ^-/σ^+ excitation at two different wavelengths into the same set of excited states: at 1987.0 meV (black) and 1987.4 meV (red). (b) PL transient under polarization switching at $B = 0$ T. PL is detected on the high energy line of X-Mn in σ^- polarization (Mn spin $S_z = -5/2$). Transient (I) (resp. (II)) was observed under resonant excitation at 1975 meV (resp. 1987 meV)

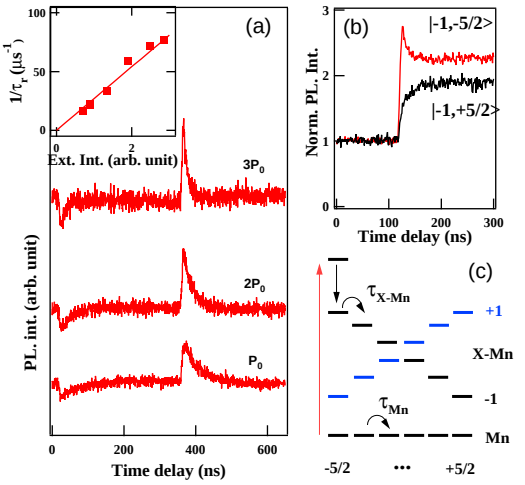

FIG. 2: (Color online) PL transients at different values of the excitation power. Inset: power dependence of the inverse response time τ_r, taken at the $1/e$ point of the spin-related transient. (b) PL transients recorded in σ^- polarization on the high (S_z=-5/2) and low (S_z=+5/2) energy line of the X-Mn complex. (c) Simplified level diagram of a Mn-doped QD, as a function of Mn spin (X-Mn: bright exciton-Mn).

dramatically depends on the excited state selected for the excitation (bottom of Fig. 1(a)): as each line corresponds to one value of the Mn spin projection S_z, that shows that the whole process creates a non-equilibrium distribution of the Mn spin states in the ground state of X-Mn. Under these conditions, switching the circular polarization of the excitation produces a change of the PL intensity (Fig. 1(b)) with two transients: first an abrupt one with the same sign for all six lines, reflecting the population change of the spin polarized excitons; then a slower transient with opposite signs on the two extreme PL lines (*i.e.*, when monitoring the Mn spin states $S_z = 5/2$ or $S_z = -5/2$, Fig. 2(b)), and a characteristic time which is inversely proportional to the pump intensity (Fig. 2(a)).

This is the signature of an optical pumping process which realizes a spin orientation of the Mn impurity. We first discuss the details of this process, then use it to study the spin dynamics of the single Mn in the QD.

The relevant sublevels of X-Mn and Mn are schematized in Fig. 2(c). For the sake of simplicity, we omit the dark exciton states which should be included for a quantitative analysis. When exciting one of the low energy excited states of the QD, two mechanisms are expected to contribute to the observed spin orientation [13]: the selective excitation of the QD can show a strong dependence on the Mn spin state, and the relaxation of the Mn spin within the X-Mn system is driven by the interaction with the spin polarized carriers which have been injected.

Under spin selective excitation, spin relaxation of X-Mn tends to empty the spin state of the Mn which gives rise to an absorption maximum [14].

Within the X-Mn complex, the spin-flip time τ_{X-Mn} is influenced by carrier-phonon, carrier-nuclei and exchange interactions affecting the exciton [14, 15]. In particular, the hole spin relaxation is controlled by the interaction with phonons [16] and can be in the ns range resulting in a partial thermalization of the X-Mn complex [12]. The off-diagonal terms of the $sp-d$ exchange interaction [11, 12] allow simultaneous spin-flips of carrier and Mn spins, and a spin transfer from the injected carriers to the localized d electrons of Mn is made possible. If these X-Mn spin-flips are faster than the spin relaxation of the Mn alone, a dynamic spin orientation of the Mn can be performed. Under injection of spin polarized carriers, this relaxation process tends to anti-align the Mn spin with the exchange field of the exciton to reach a thermal equilibrium on the X-Mn levels [14]. Hence, optical pumping with σ^- photons for instance, tends to decrease the population of the spin state S_z=-5/2 and decrease that of S_z=+5/2, as observed in Fig.2(b).

Both mechanisms, absorption selectivity and spin injection, depend on the structure of the excited states, resulting in a pumping signal which depends on the excitation energy (Fig. 1). An efficient pumping of the Mn spin can be performed within a few tens of nanoseconds, showing that at $B = 0$ the spin relaxation time of the Mn alone is long enough compared to the X-Mn dynamics.

Having established a method to prepare Mn spins, we performed pump-probe experiments to observe how the Mn polarization is conserved (Fig. 3). We prepare a non-

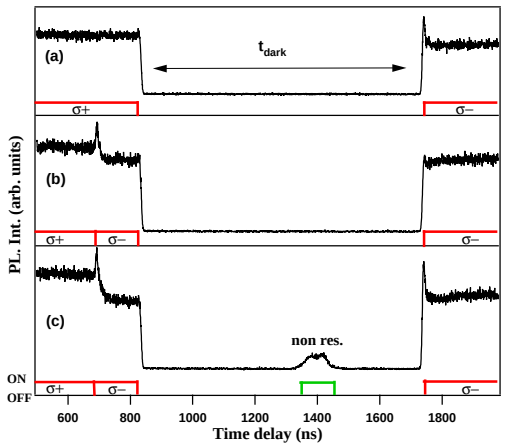

FIG. 3: (Color online) PL transients recorded under the optical polarization sequence displayed at the bottom of each plot. The spin distribution prepared by optical pumping is conserved during the dark time $t_{\rm dark}$: in (a) and (b), a transient is observed only for a different helicity of the pump and the probe (in (a), the polarization is switched during the dark time). The injection of high energy carriers with a non-resonant excitation (514 nm) forces the relaxation of the Mn spin: the optical pumping appears after $t_{\rm dark}$ (c).

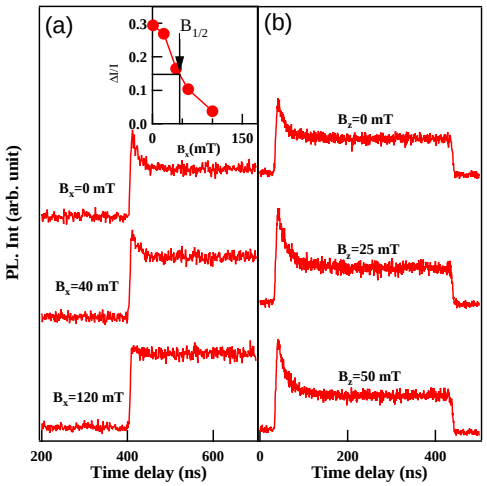

FIG. 4: (Color online) Mn spin transient as a function of a magnetic field applied in-plane (a) and out-of-plane (b). The inset in (a) shows the dependence of the transient amplitude $\Delta I/I$ (defined in Fig. 1) on the transverse field . $B_{1/2}$ corresponds to the half width at half maximum.

equilibrium distribution of the Mn spin with a $\sigma^{\pm}$ pulse. The pump laser is then switched off, and switched on again after a dark time $t_{\rm dark}$. We observe no transient if the laser is switched on with the same polarization, and a transient of constant intensity when the polarization has been changed, whatever the value of $t_{\rm dark}$ up to the μs range. This demonstrates a complete conservation of the prepared Mn spin distribution over microseconds.

In addition, as expected from previous measurements of a single Mn spin dynamics under CW optical excitation [12], the injection of high energy carriers in the vicinity of the QD significantly increases the Mn spin relaxation rate. This is illustrated in Fig. 3(c): the PL transient is recovered when free carriers have been injected during the dark time with a second non-resonant laser, thus erasing the single spin memory.

More information can be obtained from the magnetic field dependence of the optical pumping signal. For an isotropic Mn spin, the decoherence of the precessing spin gives rise to the standard Hanle depolarization curve with a Lorentzian shape and a width proportional to $1/T_2$ [6]. In the present case, a magnetic field in the Faraday configuration (B_z) does not change significantly the PL transients (Fig. 4(b)): a weak increase of the spin orientation efficiency is observed as soon as a field of a few mT is applied; above that, the pumping efficiency remains constant. By contrast, an in-plane field (B_x) induces coherent precession of the Mn spin away from the optical axis (= QDs' growth axis) , so that the average spin polarization, and therefore the amplitude of the optical pumping signal, decay (Fig. 4(a)).

It is known from electron paramagnetic resonance spectroscopy that the ground state of Mn^{2+} presents a fine structure [17]. In a cubic crystal, it results from a strong hyperfine coupling with the Mn nuclear spin, $A\,\mathbf{I}.\mathbf{S}$ (with $I = 5/2$ and $A \approx 0.7\mu$eV), and the crystal field. In addition, in epitaxial structures, built-in strains due to the lattice mismatch induce a magnetic anisotropy with an easy axis along the QD axis; it scales as $D_0 S_z^2$, with D_0 proportional to the tetragonal strain. The resulting fine structure under a magnetic field applied in-plane or out-of-plane is shown in Fig. 5(a). At zero field, the Mn electronic spin is quantized along the growth axis and the different spin doublets are split by an energy proportional to D_0.

This fine structure controls the Mn spin dynamics at zero or weak magnetic field. At zero field, in the absence of anisotropy, the precession of the electronic spin of Mn in its own hyperfine field should erase any information stored on the electronic spin [5]. In the presence of anisotropy, the precession of the Mn spin in the nuclear field is blocked even at $B = 0$. This is shown in Fig. 5(b), where we plot the evolution of the density matrix element $\rho_{5/2}(t)$, calculated for the electronic+nuclear spin system of a single Mn ion with no relaxation (*i.e.*, no coupling to the environment), with the initial condition $\rho_{5/2}(0) = 1$. With $D_0 = 0$, the coherent evolution of the electronic spin in the nuclear field erases the orientation of the electronic spin in a few 100 ps. With a D_0 of a few μeV, this free precession is blocked and the Mn spin state can be conserved for a long time, in agreement with Fig. 3. In particular, it is conserved during the time interval between the injection of two consecutive excitons,

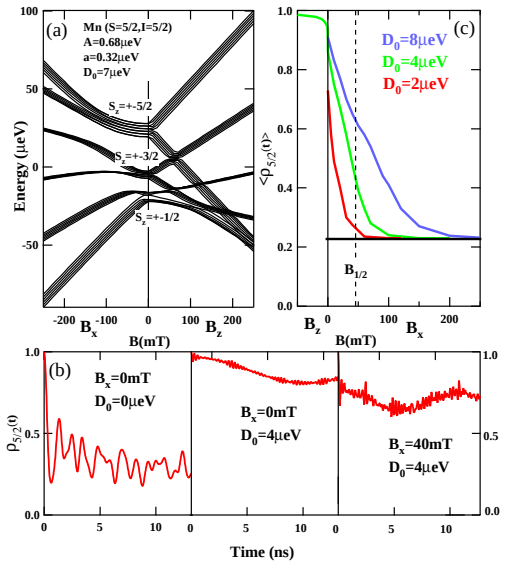

FIG. 5: (Color online) (a) Magnetic field dependence of the fine structure of the Mn spin with out-of-plane (right) and in-plane (left) field, calculated with $A = 0.68$ μeV, $D_0 = 7$ μeV and a cristal field parameter $a = 0.32$ μeV. (b) Time evolution of the density matrix element $\rho_{+5/2}(t)$ calculated for different values of D_0 and of the transverse magnetic field B_x ($\rho_{+5/2}(0) = 1$). (c) Time average value of $\langle\rho_{+5/2}(t)\rangle$ versus B_x for different values of D_0 ($T_2 = \infty$). The $B_{1/2}$ found experimentally is indicated with a dotted line.

allowing the optical pumping mechanism to take place.

The magnetic anisotropy also blocks the Mn spin precession in a weak transverse magnetic field. Then the field dependence of the optical pumping efficiency is controlled by the anisotropy D_0 and the coherence time T_2. A dephasing time $T_2^* \simeq 1$ ns has been measured in an ensemble of CdMn(2%)Se QDs [18]: a longer decoherence time T_2 is expected for a single isolated Mn spin. For $T_2 \geq 1$ ns, the influence of the decoherence on the width of the depolarization curve is smaller than 4 mT and its contribution to the experimental curve (Fig. 3(a)) can be neglected. Hence, in order to estimate D_0, we take again $T_2 = \infty$ to calculate the density matrix element $\rho_{5/2}(t)$ for $\rho_{5/2}(0) = 1$, assuming various values of D_0.

Fig. 5(c) displays the magnetic field dependence of the time-averaged value of $\rho_{5/2}(t)$. This quantity describes the probability for the state $S_z = +5/2$ to be conserved after the recombination of an exciton, as the electronic Mn spin evolves in the hyperfine field, the crystal field and the applied magnetic field. A decrease in this spin conservation progressively destroys the cumulative process controlling the optical pumping mechanism. For a free precessing spin, $\langle\rho_{5/2}(t)\rangle \approx 0.24$ as soon as a transverse field is applied and the depolarization is controlled by T_2 [6]. In the presence of anisotropy, the Mn spin does not precess at weak field and the Mn spin state is partially conserved (Fig. 5(b)). When the transverse magnetic field is strong enough to overcome the magnetic anisotropy ($g_{\rm Mn}\mu_{\rm B}B_x \gg D_0$), the time average of $\rho_{5/2}(t)$ reaches the expected value for a coherently precessing spin. This progressive decrease of $\langle\rho_{5/2}(t)\rangle$ gives rise to a field-induced depolarization curve which depends on the value of D_0. A half-height field $B_{1/2} \simeq 45$ mT, as observed experimentally in Fig. 4(b), is obtained for $D_0 \approx 6$ μeV. As a value $D_0 \approx 12$ μeV is expected for CdTe coherently grown on ZnTe [17], this is consistent with the presence of a CdZnTe alloy or a partial relaxation of the mismatch strain at the Mn location.

A magnetic anisotropy large enough to block most of the Mn spin relaxation also explains the very weak influence of an out-of-plane field. Nevertheless, the Zeeman splitting cancels the residual non-diagonal coupling induced by crystal field and slightly improves the Mn spin conservation (left part in Fig. 5(c)), thus accounting for the small increase of the optical pumping efficiency experimentally observed in Fig. 4(b).

To conclude, our results demonstrate the zero-field optical spin orientation of a single magnetic atom in a semiconductor host. Selective optical excitation of an individual Mn-doped QD with circularly polarized photons can be used to prepare a non-equilibrium distribution of the Mn spin without any applied magnetic field. Fully resonant excitation of the Mn-doped QD ground state should permit a higher fidelity preparation of the Mn spin. With this new preparation and readout scheme it should be possible to initialize a Mn spin, manipulate it on a microseconds time-scale with resonant microwave excitation and reliably read the final state.

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